(Classical) Molecular Dynamics

Outline

- Basic MD
  – Chaos
  – Shadow trajectories
  – Ergodicity

- Practical MD

- Ensembles
  – MD generates the NVE ensemble
  – The canonical NVT ensemble: thermostats

- Integrating the equations of motion
  – Verlet or velocity Verlet?
  – Liouville formulation
  – Multiple time steps

- Applications:
  – Vibrations
  – Computing transport properties

Outline

- **Basic MD**
- **– Chaos**
- **– Shadow trajectories**
- **– Ergodicity**

Molecular dynamics
Is based on Newton's equations.

$$F_i = m_i a_i = m_i \frac{d^2 x_i(t)}{dt^2}$$

for i=1 .. N particles

The force F is given by the gradient of the potential

$$F_i = -\frac{\partial V(r^N)}{\partial r_i}$$

Given the potential, one can integrate the trajectory x(t) of the whole system as a function of time.

This is an N-body problem, which can only be solved numerically (except in very special cases)
at least, in principle...

$$x(t + \Delta t) = x(t) + \dot{x}(t)\Delta t + \frac{1}{2}\ddot{x}(t)\Delta t^2 + \frac{1}{6}\dddot{x}(t)\Delta t^3 + \ldots$$

Naïve implementation: truncation of Taylor expansion

$$x(t + \Delta t) = x(t) + \dot{x}(t)\Delta t + \frac{1}{2}\ddot{x}(t)\Delta t^2$$

Wrong!
The naive "forward Euler" algorithm
• is not time reversible
• does not conserve volume in phase space
• suffers from energy drift
Better approach: "Verlet" algorithm

Verlet algorithm
compute position in next and previous time steps

$$x(t + \Delta t) = x(t) + \dot{x}(t)\Delta t + \frac{1}{2}\ddot{x}(t)\Delta t^2 + \frac{1}{6}\dddot{x}(t)\Delta t^3 + \frac{1}{24}\ddddot{x}(t)\Delta t^4...$$

$$x(t - \Delta t) = x(t) - \dot{x}(t)\Delta t + \frac{1}{2}\ddot{x}(t)\Delta t^2 - \frac{1}{6}\dddot{x}(t)\Delta t^3 + \frac{1}{24}\ddddot{x}(t)\Delta t^4...$$

$$x(t + \Delta t) + x(t - \Delta t) = 2x(t) + \ddot{x}(t)\Delta t^2 + \mathcal{O}(\Delta t^4)...$$

Or $\quad x(t + \Delta t) = 2x(t) - x(t - \Delta t) + \ddot{x}(t)\Delta t^2$
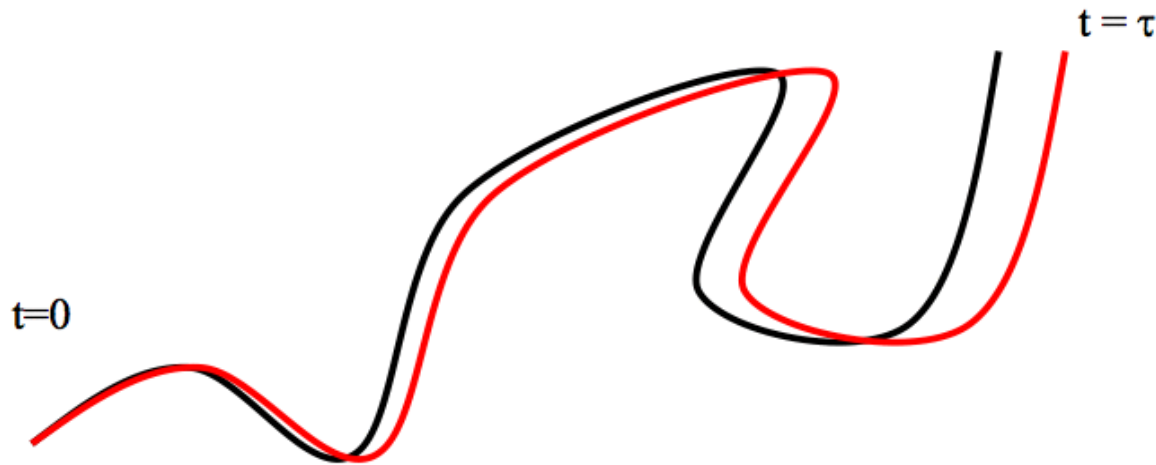
Verlet algorithm:
– is time reversible
– does conserve volume in phase space, i.e., it is "symplectic"
(conservation of "action element" $dp \wedge dq$)
– does not suffer from energy drift
...but is it a good algorithm?
i.e. does it predict the time evolution of the system correctly???

Molecular chaos

Dynamics of "well-behaved" classical many-body system is chaotic.
Consequence: Trajectories that differ very slightly in their initial
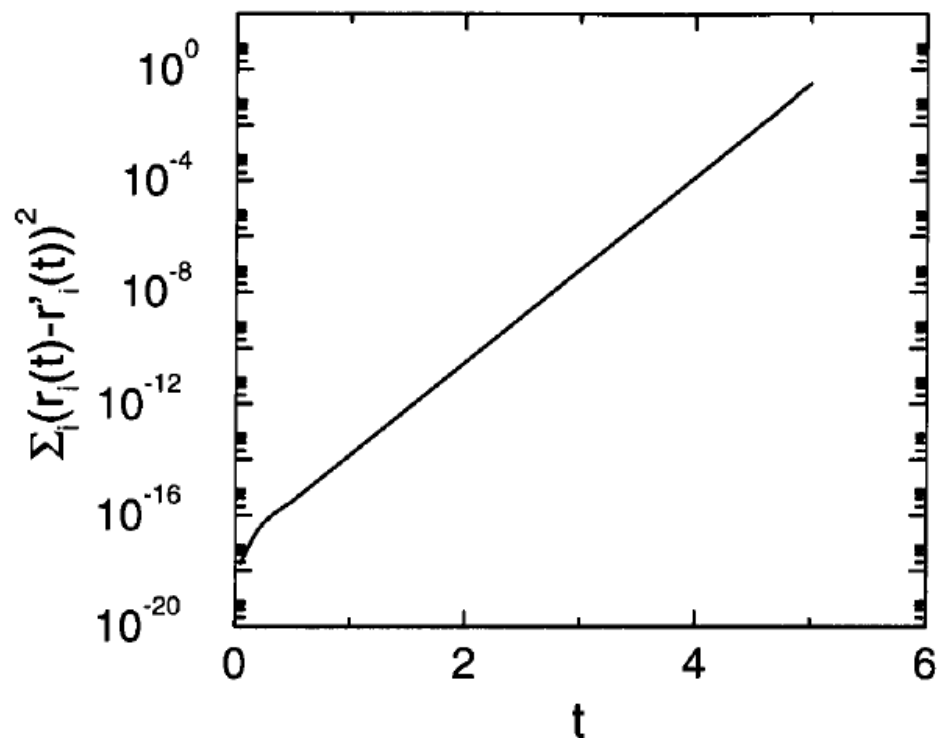conditions diverge exponentially ("Lyapunov instability")

$$\mathbf{r}(t) = f\left[\mathbf{r}^N(0), \mathbf{p}^N(0); t\right]$$

$$\mathbf{r}'(t) = f\left[\mathbf{r}^N(0), \mathbf{p}^N(0) + \boldsymbol{\epsilon}; t\right]$$

$$|\Delta \mathbf{r}(t)| \sim \epsilon \exp(\lambda t)$$

$$\epsilon \sim \Delta_{max} \exp(-\lambda t_{max})$$

Why should anyone believe Molecular Dynamics simulations ???

Why should anyone believe Molecular Dynamics simulations ???

Answers:

1. Good MD algorithms (e.g. Verlet) can also be considered as good (*NVE*!) Monte Carlo algorithm – they therefore yield reliable STATIC properties ("Hybrid Monte Carlo")

2. What is the point of simulating dynamics, if we cannot trust the resulting time-evolution???

3. All is well (probably), because of… The Shadow Theorem.

Shadow theorem (hypothesis)

• For any realistic many-body system, the shadow theorem is merely a hypothesis.

• It basically states that good algorithms generate numerical trajectories that are "close to" a REAL trajectory of the many-body system.

• Question: Does the Verlet algorithm indeed generate "shadow" trajectories?

• In practice, it follows an Hamiltonian, depending on the timestep, $\tilde{\mathcal{H}}(\mathbf{x}, \Delta t)$ which is close to the real Hamiltonian $\mathcal{H}(\mathbf{x})$, in the sense that for $\Delta t \longrightarrow 0$ $\tilde{\mathcal{H}}(\mathbf{x}, \Delta t)$ converges to $\mathcal{H}(\mathbf{x})$

• Take a different look at the problem.

– Do not discretize NEWTON's equation of motion…

– …but discretize the ACTION

Lagrangian Classical mechanics

- Newton:

$$F(x, t) = m\ddot{x}$$

- Lagrange (variational formulation of classical mechanics):

– Consider a system that is at a point r_0 at time 0 and at point r_t at time t, then the system follows a trajectory $r(t)$ such that:

$$S = \int_{t_b}^{t_e} dt \, [\mathcal{K} - \mathcal{U}]$$

is an extremum.

Lagrangian approach

$$\mathcal{L}(\dot{r}, r) = K(\dot{r}) - U(r) = \frac{m\dot{r}^2}{2} - U(r)$$

$$\frac{\partial \mathcal{L}}{\partial \dot{r}} = \frac{\partial K}{\partial \dot{r}} = p \qquad \frac{\partial \mathcal{L}}{\partial r} = -\frac{\partial U}{\partial r} = F$$

$$p = \frac{\partial \mathcal{L}(\dot{r}, r)}{\partial \dot{r}} \qquad \dot{p} = \frac{\partial \mathcal{L}(\dot{r}, r)}{\partial r}$$

Lagrangian

For example, if we use Cartesian coordinates:

$$\mathcal{L}(r(t)) = \sum_{i=1}^{N} \frac{1}{2} m_i \dot{r}_i^2 - U(r_1, r_2, \ldots r_N)$$

Consider the "true" path $R(t)$, with $R(0)=r_0$ and $R(t)=r_t$.
Now, consider a path close to the true path:

$$r(t') = R(t') + \delta r(t')$$

Then the action S is an extremum if

$$\frac{\partial S}{\partial r(t')} = 0 \ \text{ for all } t$$

what does this mean?

Shadow trajectory

Discretized action

$$S_{cont} = \int_{t_0}^{t_1} dt \mathcal{L}(t)$$

$$S_{disc} = \Delta t \sum_{i=0}^{i_{max}} \mathcal{L}(t_i)$$

$$\mathcal{L}(t_i) = K(t_i) - U(t_i)$$

For a one dimensional system this becomes

$$\mathcal{L}(t_i)\Delta t = \frac{1}{2} m \Delta t \frac{(x_{i+1} - x_i)^2}{\Delta t^2} - U(x_i)\Delta t$$

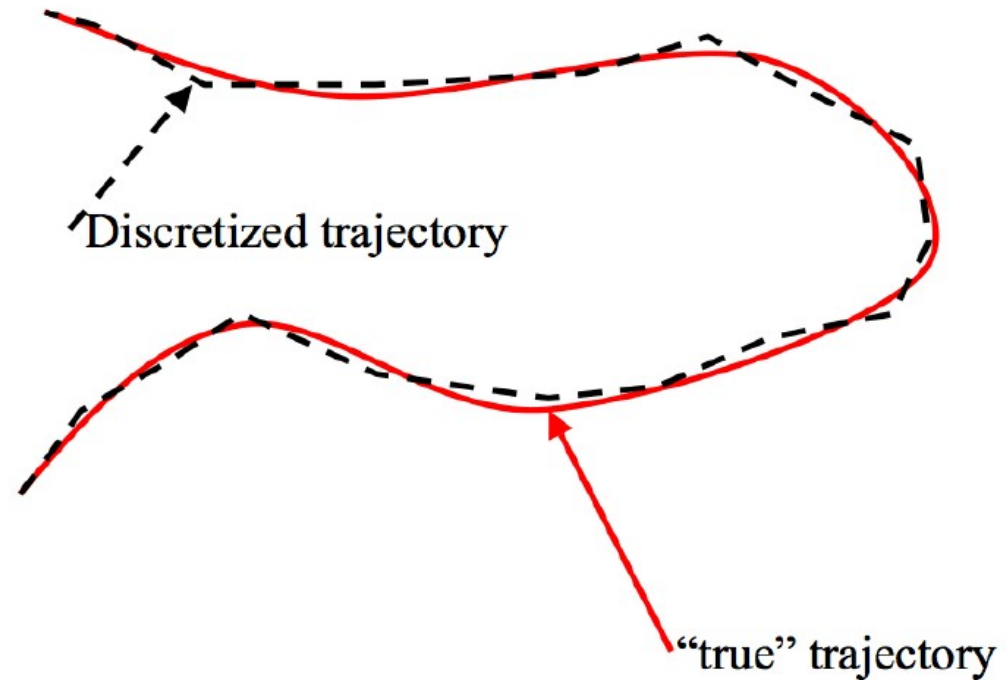$$S_{disc} = \sum_{i=1}^{i_{max}} \left[\frac{m(x_{i+1} - x_i)^2}{2\Delta t} - U(x_i)\Delta t \right]$$

Minimize the action
Now do the standard thing: Find the extremum for small variations in the path, i.e. for small variations in all xi.

$$\frac{\partial S_{disc}}{\partial x_i} = 0 \ \text{ for all } i$$

This will generate a discretized trajectory that starts at time t_0 at X_0, and ends at time t at X_t.

Discretized trajectory

"true" trajectory

$$\frac{\partial S_{disc}}{\partial x_i} = \frac{\partial}{\partial x_i} \sum_{i=1}^{i_{max}} \left[\frac{m(x_{i+1} - x_i)^2}{2\Delta t} - U(x_i)\Delta t \right]$$

$$\frac{\partial S_{disc}}{\partial x_i} = \frac{-m(x_{i+1} - x_i) + m(x_i - x_{i-1})}{\Delta t} - \Delta t \frac{\partial U(x_i)}{\partial x_i}$$

$$0 = \frac{m}{\Delta t} \left(2x_i - x_{i+1} - x_{i-1} - \frac{\Delta t^2}{m} \frac{\partial U(x_i)}{\partial x_i} \right)$$

Minimizing the action

$$0 = 2x_i - x_{i+1} - x_{i-1} - \frac{\Delta t^2}{m} \frac{\partial U(x_i)}{\partial x_i}$$

$$x_{i+1} = 2x_i - x_{i-1} + \frac{\Delta t^2}{m} F(x_i)$$

- which is the Verlet algorithm!
- The Verlet algorithm generates a trajectory that satisfies the boundary conditions of a REAL trajectory –both at the beginning and at the endpoint.
- Hence, if we are interested in statistical information about the dynamics
(e.g. time-correlation functions, transport coefficients, power spectra...)
...then a "good" MD algorithm (e.g. Verlet) is fine.

Yes, but: ergodicity

$$\rho_i(r; \mathbf{r}^N(0), \mathbf{p}^N(0), t) \to \overline{\rho_i(r)}$$

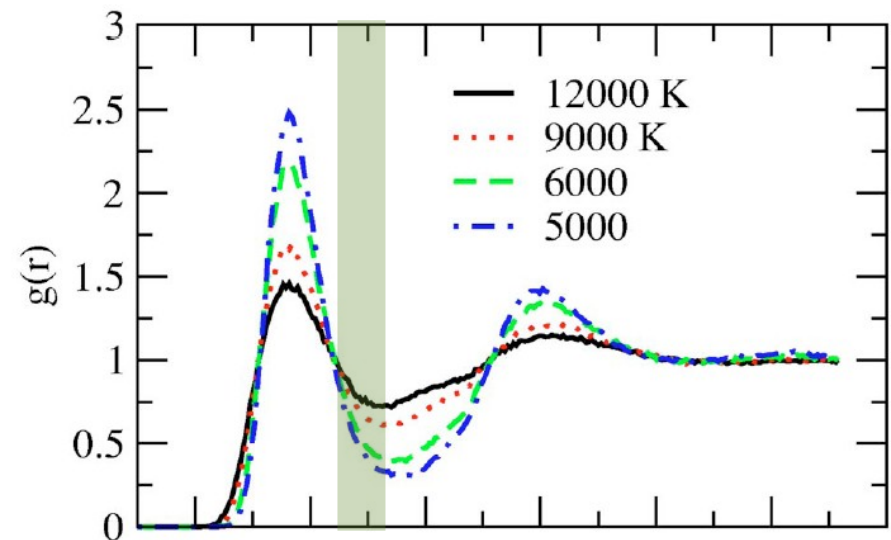$$\overline{\rho_i(r)} = \lim_{t\to\infty} \frac{1}{t} \int_0^t dt' \rho_i(r, t')$$
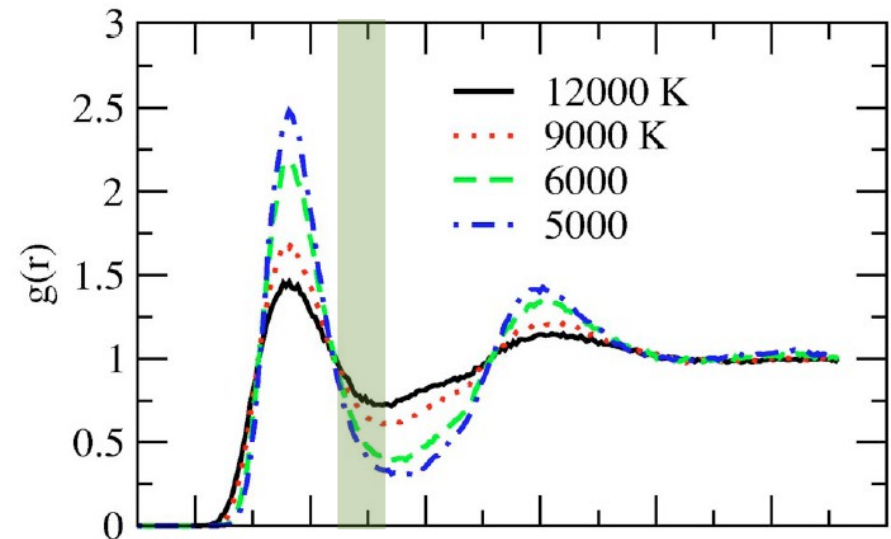
$$= \frac{\sum_{\text{initial conditions}} \left(\lim_{t\to\infty} \frac{1}{t} \int_0^t dt' \rho_i(r, \mathbf{r}^N(0), \mathbf{p}^N(0), t') \right)}{\text{number of initial conditions}}$$

Yes, but: ergodicity

$$\frac{\sum_{\text{initial conditions}} f\left(\mathbf{r}^N(0), \mathbf{p}^N(0)\right)}{\text{number of initial conditions}} \longrightarrow \frac{\int_E f\left(\mathbf{r}^N(0), \mathbf{p}^N(0)\right)}{\Omega(N, V, E)}$$

$$\overline{\rho_i(r)} = \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' \rho_i(r, t')$$

$$= \lim_{t \to \infty} \frac{1}{t} \int_0^t dt' \left\langle \rho_i(r, \mathbf{r}^N(0), \mathbf{p}^N(0), t') \right\rangle_{NVE} = \left\langle \rho_i(r) \right\rangle_{NVE}$$

1. Read essential parameters (temperature, # of atoms, time step, etc.)

2. Initialize system – positions and velocities

3. Evaluate forces

4. Integrate equations of motion

Central loop

5. Stop after a given time – enough statistics for your measurement

Algorithm 3 (A Simple Molecular Dynamics Program)

```
program md                      simple MD program

call init                       initialization
t=0
do while (t.lt.tmax)            MD loop
    call force(f,en)            determine the forces
    call integrate(f,en)        integrate equations of motion
    t=t+delt
    call sample                 sample averages
enddo
stop
end
```

```
subroutine init                    initialization of MD program
sumv=0
sumv2=0
do i=1,npart
   x(i)=lattice_pos(i)             place the particles on a lattice
   v(i)=(ranf()-0.5)               give random velocities
   sumv=sumv+v(i)                  velocity center of mass
   sumv2=sumv2+v(i)**2             kinetic energy
enddo
sumv=sumv/npart                    velocity center of mass
sumv2=sumv2/npart                  mean-squared velocity
fs=sqrt(3*temp/sumv2)              scale factor of the velocities
do i=1,npart                       set desired kinetic energy and set
   v(i)=(v(i)-sumv)*fs             velocity center of mass to zero
   xm(i)=x(i)-v(i)*dt              position previous time step
enddo
return
end
```

$$\frac{3}{2}k_B T = \frac{1}{2}mv^2$$

Evaluation of forces (in *ab initio* MD this is the expensive part)

```
subroutine force(f,en)              determine the force
en=0                                and energy
do i=1,npart
    f(i)=0                          set forces to zero
enddo
do i=1,npart-1
  do j=i+1,npart                    loop over all pairs
      xr=x(i)-x(j)
      xr=xr-box*nint(xr/box)        periodic boundary conditions
      r2=xr**2
      if (r2.lt.rc2) then           test cutoff
        r2i=1/r2
        r6i=r2i**3
        ff=48*r2i*r6i*(r6i-0.5)     Lennard-Jones potential
        f(i)=f(i)+ff*xr             update force
        f(j)=f(j)-ff*xr
        en=en+4*r6i*(r6i-1)-ecut    update energy
      endif
  enddo
enddo
return
end
```

Integrator (Verlet)

```fortran
subroutine integrate(f,en)          integrate equations of motion
sumv=0
sumv2=0
do i=1,npart                        MD loop
    xx=2*x(i)-xm(i)+delt**2*f(i)    Verlet algorithm (4.2.3)
    vi=(xx-xm(i))/(2*delt)          velocity (4.2.4)
    sumv=sumv+vi                    velocity center of mass
    sumv2=sumv2+vi**2               total kinetic energy
    xm(i)=x(i)                      update positions previous time
    x(i)=xx                         update positions current time
enddo
temp=sumv2/(3*npart)                instantaneous temperature
etot=(en+0.5*sumv2)/npart           total energy per particle
return
end
```

$$T = \frac{\langle 2K \rangle}{k_B 3N}$$

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– Liouville formulation
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- Applications

- Initialization
– Total momentum should be zero (no external forces)
– Temperature rescaling to desired temperature
– Particles/atoms/molecules start on a lattice or random positions

- Force calculations
– Periodic boundary conditions
– Straightforward force: Order N^2 algorithm:
– neighbor lists, linked cell: Order N
– Electrostatics: Ewald summation $O(N^{1.5})$

- Integrating the equations of motion
– Controlling the temperature by a Thermostat
– Verlet or velocity Verlet?
– Multiple time steps

Clusters ARE different from bulk
Surface! In a cube of length L, one particle per unit length :
$[L^3-(L-2)^3]/L^3 \sim 6L^2/L^3$
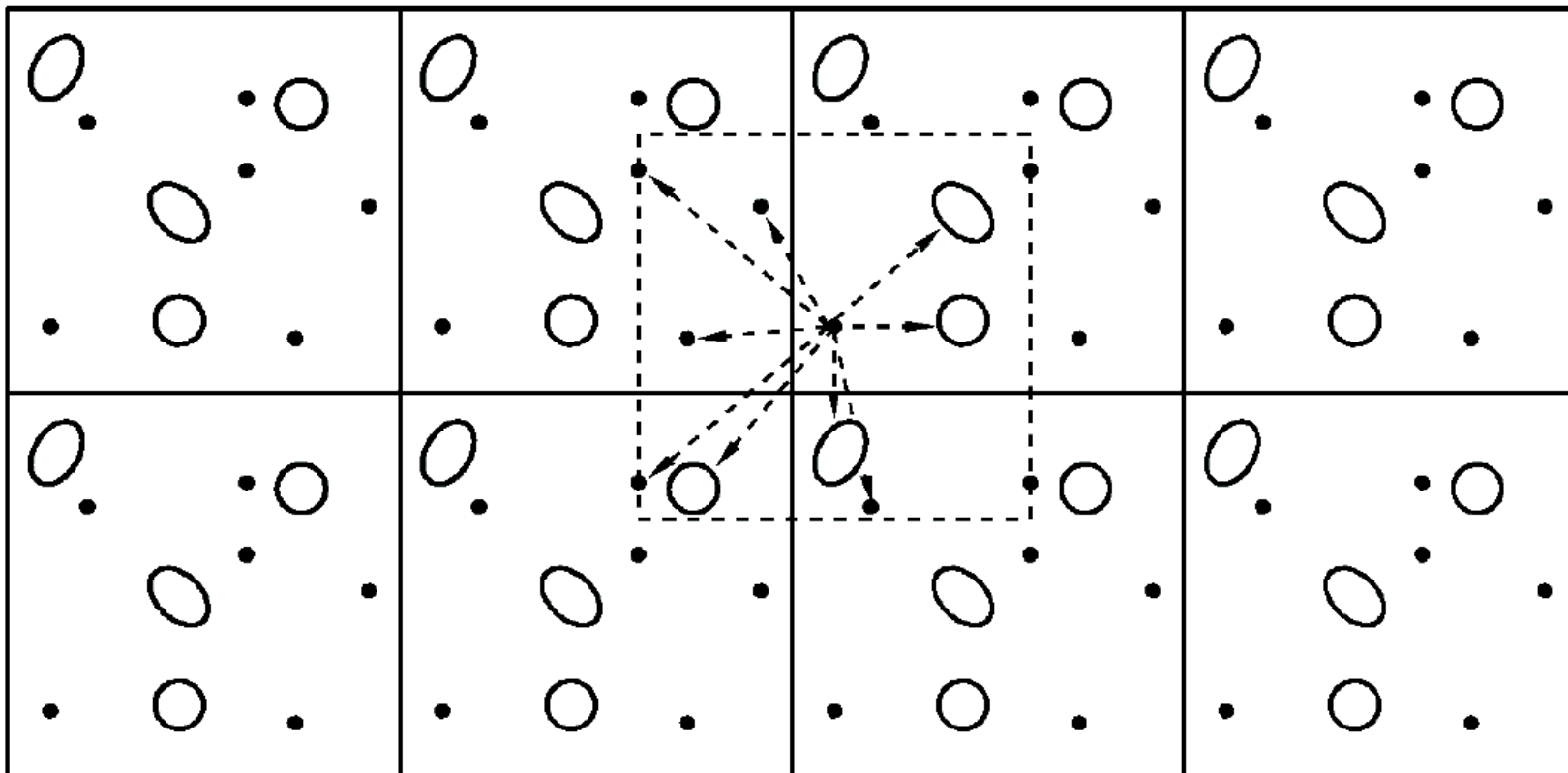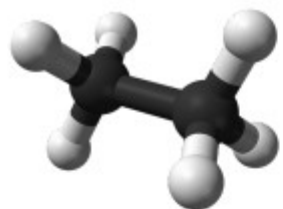
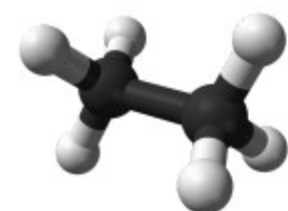Energy fluctuations (arbitrary shifts)
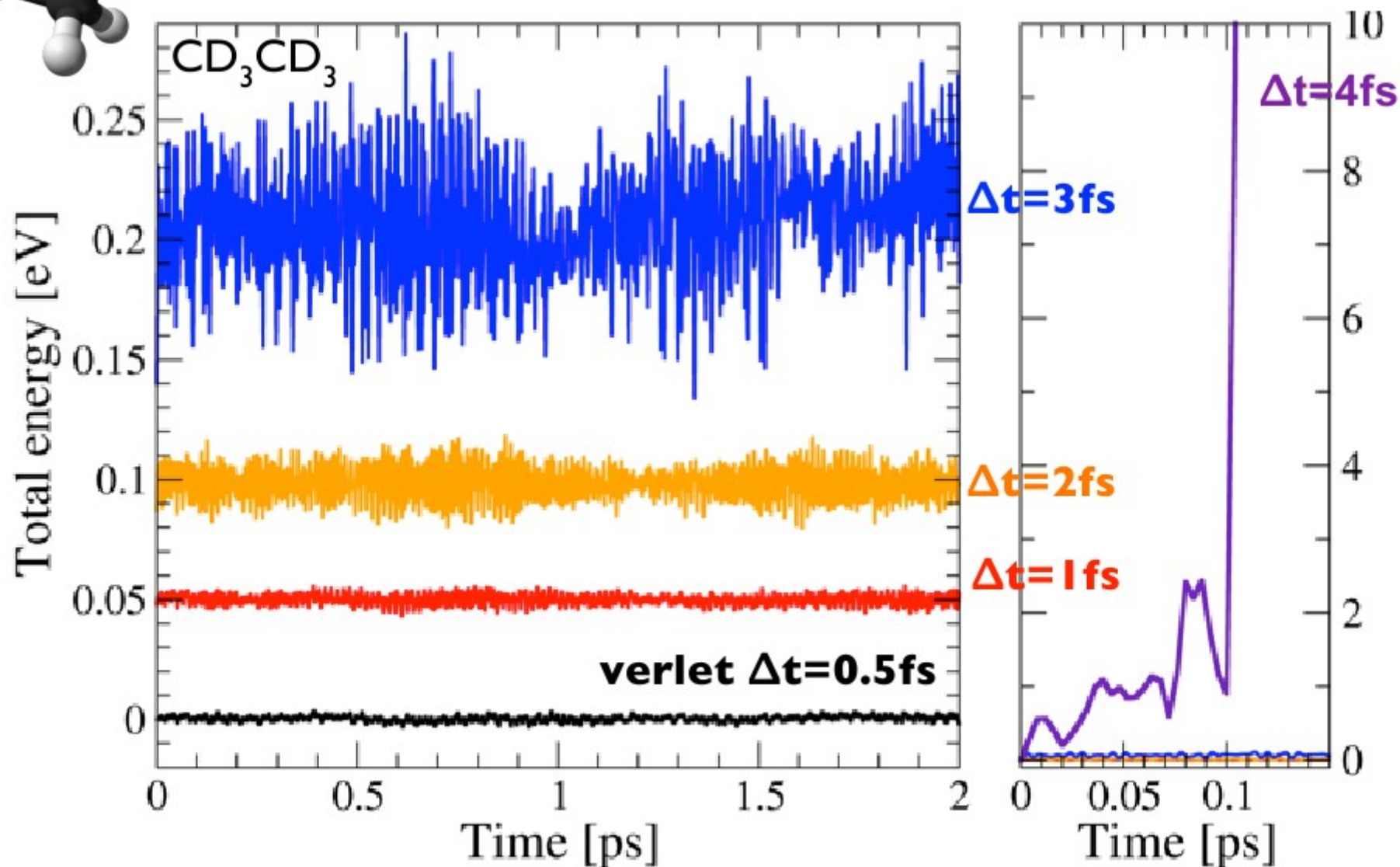
Energy fluctuations (arbitrary shifts)

CD_3CD_3

0.25

$\Delta t=4fs$

10
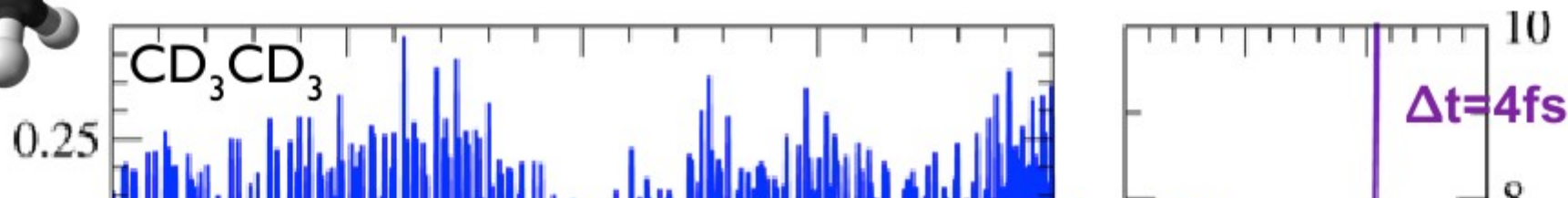
- What is a good time step?

  - Depends on the highest vibrational frequency (thus mass) of your system ($\omega \approx \sqrt{k/M}$)

  - Typically, choose a time step corresponding to ~$1/(10\omega_{max})$ (femtosecond time scale)
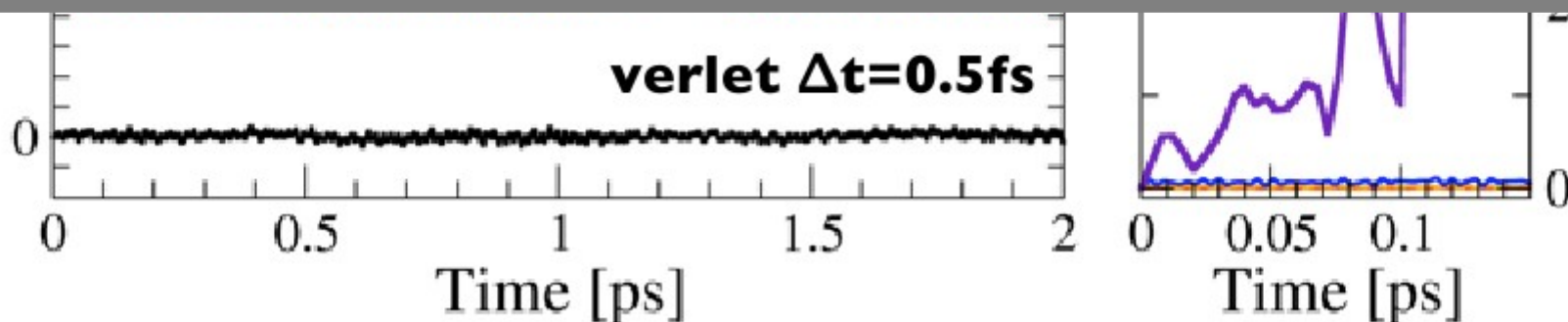
verlet $\Delta t=0.5fs$

0

0   0.5   1   1.5   2   0   0.05   0.1

Time [ps]   Time [ps]

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Lagrangian approach

$$\mathcal{L}(\dot{r}, r) = K(\dot{r}) - U(r) = \frac{m\dot{r}^2}{2} - U(r)$$

$$\frac{\partial \mathcal{L}}{\partial \dot{r}} = \frac{\partial K}{\partial \dot{r}} = p \qquad \frac{\partial \mathcal{L}}{\partial r} = -\frac{\partial U}{\partial r} = F$$

$$p = \frac{\partial \mathcal{L}(\dot{r}, r)}{\partial \dot{r}} \qquad \dot{p} = \frac{\partial \mathcal{L}(\dot{r}, r)}{\partial r}$$

Hamiltonian approach

The Hamiltonian is defined as

$$H(p, r) = p\dot{r} - \mathcal{L}(\dot{r}, r)$$

$$H(p^N, r^N) = U(r^N) + \sum_i \frac{p_i^2}{2m_i} = U + K$$

Hamilton's equations are then

$$\dot{r} = \frac{\partial \mathcal{H}(r, p)}{\partial p} = \frac{p}{m}$$

$$\dot{p} = -\frac{\partial \mathcal{H}(r, p)}{\partial r} = -\frac{\partial U(r^N)}{\partial r}$$

Integrating equations of motion (by Verlet) conserves the Hamiltonian

Conservation of the Hamiltonian

$$dH(p,r) = \frac{\partial H}{\partial p}dp + \frac{\partial H}{\partial r}dr$$

$$\frac{\partial H}{\partial p} = \dot{r} \qquad \frac{\partial H}{\partial r} = -\dot{p}$$

$$\frac{dH(p,r)}{dt} = \frac{\partial H}{\partial p}\dot{p} + \frac{\partial H}{\partial r}\dot{r} = \dot{r}\dot{p} - \dot{p}\dot{r} = 0$$

A solution to Hamilton's equations conserves the TOTAL energy

$$E = U + K$$

MD samples the microcanonical (*NVE*) ensemble

- The idea: couple the system to a thermostat (heat bath)
- Interesting because:
  - Experiments are usually done at constant temperature
  - Better modeling of conformational changes

Bath

System

Energy is conserved

Energy is not conserved

Introduce thermostat in MD trajectory:

- deterministic thermostat
– Nose-Hoover (1984)
– Nose-Hoover chains (Martyna et al. 1992)

- stochastic thermostats
– Andersen
– Langevin
– Nose-Hoover-Langevin (Leimkuhler et al, 2009)
– Stochastic Velocity rescaling (Bussi-Donadio-Parrinello, 2007)

All of these alter the velocities such that the trajectory samples the canonical NVT ensemble, and the partition function becomes

$$Z = \frac{1}{N! \Lambda^{3N}} \int e^{-\beta \mathcal{U}(r)} dr$$

These thermostats differ in how they achieve this

Probability distribution of the kinetic energy:

$$P(E_{kin}) \propto \exp(-E_{kin}/k_B T)$$

Maxwell-Boltzmann-Distribution

$$T < T < T$$
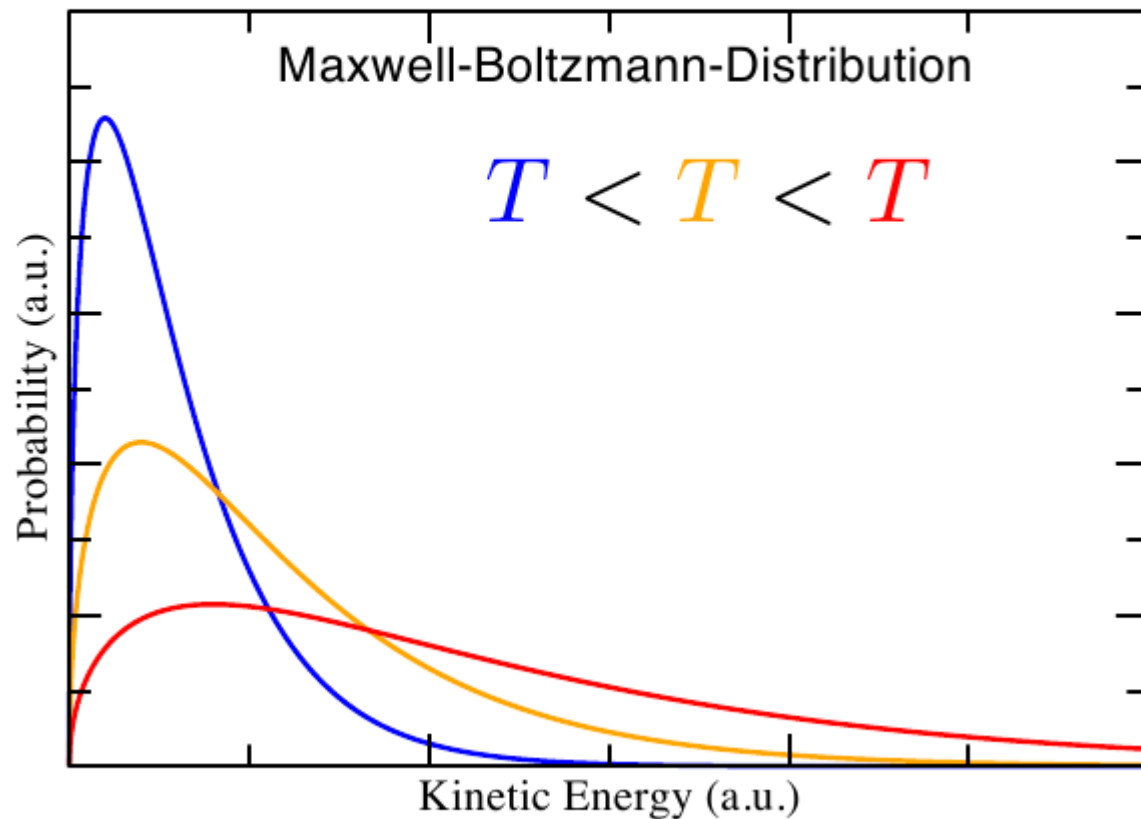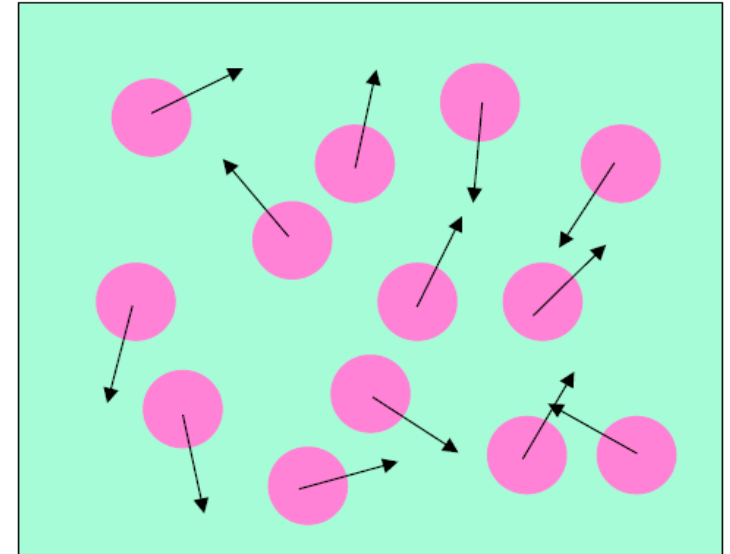
kinetic
energy: $p^2/2M$

$$T = \frac{2\langle E_{kin} \rangle}{3 N k_B}$$

# of particles

Andersen thermostat

• Every particle has a fixed probability to collide with the Andersen demon

• After collision the particle is give a new Velocity

$$P(v) = \left(\frac{\beta}{2\pi m}\right)^{3/2} \exp\left[-\beta m v^2 / 2\right]$$

• The probabilities to collide are uncorrelated (Poisson distribution)

$$P(t;v) = v \exp\left[-vt\right]$$

• Downside: momentum not conserved. Fixed by Lowe-Andersen (2006)

goal: compute MD trajectory sampling NVT ensemble.
Take kinetic energy out of the system and store it into a reservoir
The reservoir can be seen as additional variable s that "stores" kinetic energy
Approach: extended phase space

extended variable

$$\mathcal{H}_N = \sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i s^2} + U(\mathbf{r}_1, ..., \mathbf{r}_N) + \frac{p_s^2}{2Q} + gkT \ln s,$$

constant to be set

Original system

effective mass

Fictitious oscillator

$$\Omega = \int d^N \mathbf{r} \, d^N \mathbf{p} \, ds \, dp_s \; \delta \left(\sum_{i=1}^{N} \frac{\mathbf{p}_i^2}{2m_i s^2} + U(\mathbf{r}_1, ..., \mathbf{r}_N) + \frac{p_s^2}{2Q} + gkT \ln s - E \right)$$

Change of variable:

$$\tilde{\mathbf{p}}_i = \frac{\mathbf{p}_i}{s}$$

Justification of Nosé thermostat

$$\Omega = \int d^N\mathbf{r}\, d^N\tilde{\mathbf{p}}\, ds\, dp_s\, s^{dN}\delta\left(\sum_{i=1}^{N}\frac{\tilde{\mathbf{p}}_i^2}{2m_i} + U(\mathbf{r}_1,...,\mathbf{r}_N) + \frac{p_s^2}{2Q} + gkT\ln s - E\right)$$

$$= \int d^N\mathbf{r}\, d^N\mathbf{p}\, ds\, dp_s\, s^{dN}\delta\left(\mathcal{H}(\mathbf{r},\mathbf{p}) + \frac{p_s^2}{2Q} + gkT\ln s - E\right)$$

Hamiltonian of the atomic (sub)system $\quad \mathcal{H} = \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1,...,\mathbf{r}_N)$

$$\delta(f(s)) = \frac{\delta(s-s_0)}{|f'(s_0)|} \qquad f(s) = \mathcal{H}(\mathbf{r},\mathbf{p}) + p_s^2/2Q + gkT\ln s - E$$

$$f(s_0) = 0: \quad s_0 = e^{(E-\mathcal{H}(\mathbf{r},\mathbf{p})-p_s^2/2Q)/gkT} \quad \Rightarrow \quad \frac{1}{|f'(s_0)|} = \frac{1}{gkT}e^{(E-\mathcal{H}(\mathbf{r},\mathbf{p})-p_s^2/2Q)/gkT}$$

$$\Omega = \frac{1}{gkT}\int d^N\mathbf{p}\, d^N\mathbf{r}\, dp_s\, e^{(dN+1)(E-\mathcal{H}(\mathbf{r},\mathbf{p})-p_s^2/2Q)/gkT} \qquad \text{if: } g = dN+1$$
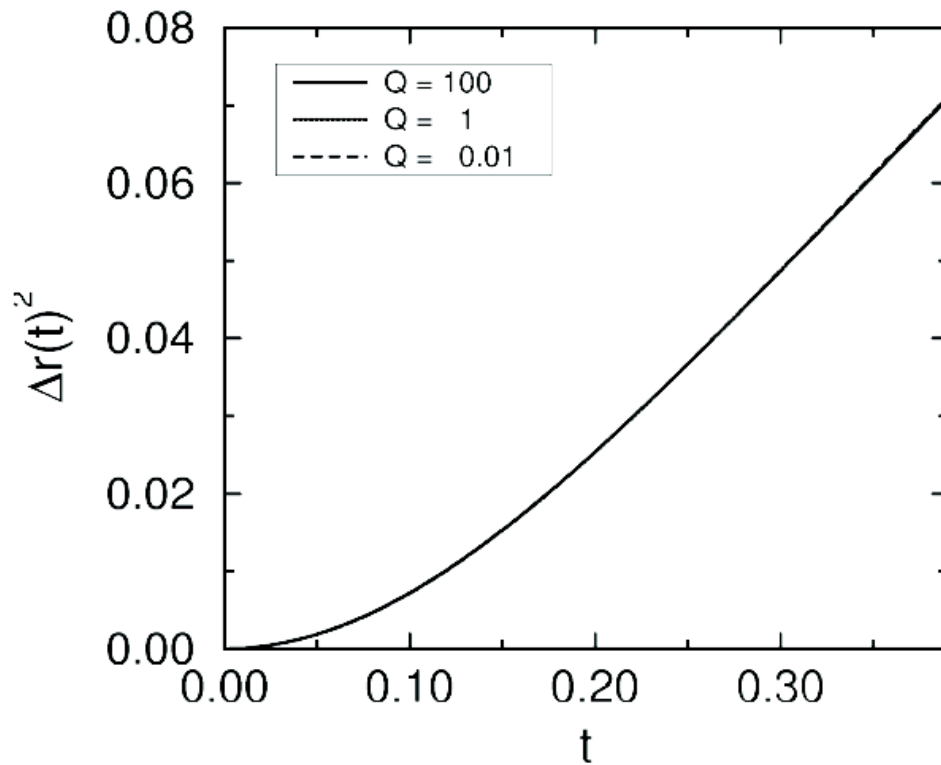
$$\Omega = \frac{e^{E/kT}\sqrt{2\pi QkT}}{(dN+1)kT}\int d^N\mathbf{p}\, d^N\mathbf{r}\, e^{-\mathcal{H}(\mathbf{r},\mathbf{p})/kT}$$

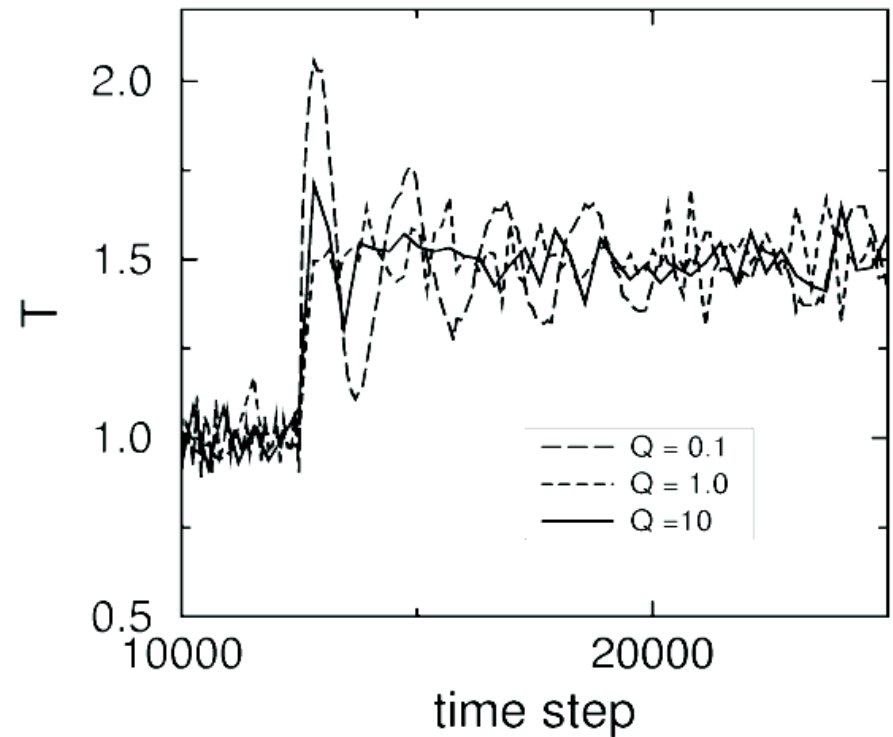Which is (proportional to) the canonical partition function for

$$\mathcal{H} = \sum_{i=1}^{N}\frac{\mathbf{p}_i^2}{2m_i} + U(\mathbf{r}_1,...,\mathbf{r}_N)$$

Lennard-Jones fluid

mean square displacement

temperature relaxation

Combine concepts from velocity rescaling (fast!) with concepts from stochastic thermostats (accurate!)

Target temperature follows a stochastic differential equation:

$$\frac{dT}{\bar{T}} = \left[1 - \frac{T(t)}{\bar{T}}\right]\frac{dt}{\tau} - 2\sqrt{\frac{T(t)}{3\bar{T}N\tau}}\xi(t)$$

Stochastic velocity rescaling thermostat

Combine concepts from velocity rescaling (fast!) with concepts from stochastic thermostats (accurate!)

Target temperature follows a stochastic differential equation:

$$\frac{dT}{\bar{T}} = \boxed{\left[1 - \frac{T(t)}{\bar{T}} \right] \frac{dt}{\tau}} \boxed{2\sqrt{\frac{T(t)}{3\bar{T}N\tau}}\xi(t)}$$

Temperature rescaling   White noise

- Very successful thermostat, weakly dependent on relaxation time τ
- Pseudo-Hamiltonian is conserved

Outline

Verlet algorithm

$$\mathbf{r}(t + \Delta t) \approx 2\mathbf{r}(t) - \mathbf{r}(t - \Delta t) + \frac{\Delta t^2}{m}\mathbf{f}(t)$$

Downside regular verlet algorithm: velocity is not known.

Velocity verlet (Andersen 1983):

$$\mathbf{r}(t + \Delta t) \approx \mathbf{r}(t) + \mathbf{v}(t)\Delta t + \frac{\Delta t^2}{2m}\mathbf{f}(t)$$

$$\mathbf{v}(t + \Delta t) \approx \mathbf{v}(t) + \frac{\Delta t}{2m}\left[\mathbf{f}(t + \Delta t) + \mathbf{f}(t)\right]$$

Is based on Trotter decomposition of Liouville operator formulation, also basis of Multiple time steps, and modern thermostats such as the Nose-Hoover-Langevin.

Liouville formulation

$$a(\mathbf{x}) \qquad \frac{\mathrm{d}a}{\mathrm{d}t} = \sum_{\alpha=1}^{3N} \left[\frac{\partial a}{\partial q_\alpha} \dot{q}_\alpha + \frac{\partial a}{\partial p_\alpha} \dot{p}_\alpha \right] \qquad \dot{q}_\alpha = \frac{\partial \mathcal{H}}{\partial p_\alpha} \qquad \dot{p}_\alpha = -\frac{\partial \mathcal{H}}{\partial q_\alpha}$$

(implicit dependence on *t*)

$$\frac{\mathrm{d}a}{\mathrm{d}t} = \sum_{\alpha=1}^{3N} \left[\frac{\partial a}{\partial q_\alpha} \frac{\partial \mathcal{H}}{\partial p_\alpha} - \frac{\partial a}{\partial p_\alpha} \frac{\partial \mathcal{H}}{\partial q_\alpha} \right] \qquad iL = \sum_{\alpha=1}^{3N} \left[\frac{\partial \mathcal{H}}{\partial p_\alpha} \frac{\partial}{\partial q_\alpha} - \frac{\partial \mathcal{H}}{\partial q_\alpha} \frac{\partial}{\partial p_\alpha} \right]$$

Definition of operator *L*

Formal solution (useless, unless…)

$$a(\mathbf{x}_t) = \mathrm{e}^{iLt} a(\mathbf{x}_0)$$

A choice for *a(x)*

$$\mathrm{a}(\mathbf{x}) = \mathbf{x} \implies \mathbf{x}_t = \mathrm{e}^{iLt} \mathbf{x}_0$$

$$iL = iL_1 + iL_2 \qquad iL_1 = \sum_{\alpha=1}^{N} \frac{\partial \mathcal{H}}{\partial p_\alpha} \frac{\partial}{\partial q_\alpha} \qquad iL_2 = -\sum_{\alpha=1}^{N} \frac{\partial \mathcal{H}}{\partial q_\alpha} \frac{\partial}{\partial p_\alpha}$$

$$iL_1 iL_2 \phi(\mathbf{x}) \neq iL_2 iL_1 \phi(\mathbf{x})$$

Liouville formulation

$$iL_1 = \sum_{\alpha=1}^{N} \frac{\partial \mathcal{H}}{\partial p_\alpha} \frac{\partial}{\partial q_\alpha} \qquad iL_2 = -\sum_{\alpha=1}^{N} \frac{\partial \mathcal{H}}{\partial q_\alpha} \frac{\partial}{\partial p_\alpha}$$

$$\mathcal{H} = \frac{p^2}{2m} + U(x) \qquad iL_1 = \frac{p}{m} \frac{\partial}{\partial x} \qquad iL_2 = F(x) \frac{\partial}{\partial p} \qquad F(x) = -\mathrm{d}U/\mathrm{d}x$$

L_1 and L_2 do not commute:

$$iL_1 iL_2 \quad \phi(x,p) \qquad \frac{p}{m} \frac{\partial}{\partial x} F(x) \frac{\partial}{\partial p} \phi(x,p) = \frac{p}{m} F(x) \frac{\partial^2 \phi}{\partial p \partial x} + \frac{p}{m} F'(x) \frac{\partial \phi}{\partial p}$$

$$iL_2 iL_1 \quad \phi(x,p) \qquad F(x) \frac{\partial}{\partial p} \frac{p}{m} \frac{\partial}{\partial x} \phi(x,p) = F(x) \frac{p}{m} \frac{\partial^2 \phi}{\partial p \partial x} + F(x) \frac{1}{m} \frac{\partial \phi}{\partial x}$$

$$[iL_1, iL_2]\phi(x,p) = \frac{p}{m} F'(x) \frac{\partial \phi}{\partial p} - \frac{F(x)}{m} \frac{\partial \phi}{\partial x}$$

Trotter decomposition in general:

$$[A, B] \neq 0 \qquad e^{A+B} = \lim_{P \to \infty} \left[e^{B/2P} e^{A/P} e^{B/2P} \right]^P$$

For $iL = iL_1 + iL_2$:

$$e^{iLt} = e^{(iL_1 + iL_2)t} = \lim_{P \to \infty} \left[e^{iL_2 t/2P} e^{iL_1 t/P} e^{iL_2 t/2P} \right]^P$$

Introducing the small, discrete time step Δt:

$$\Delta t = t/P \qquad e^{iLt} = \lim_{P \to \infty, \Delta t \to 0} \left[e^{iL_2 \Delta t/2} e^{iL_1 \Delta t} e^{iL_2 \Delta t/2} \right]^P$$

$$e^{iLt} \approx \left[e^{iL_2 \Delta t/2} e^{iL_1 \Delta t} e^{iL_2 \Delta t/2} \right]^P + \mathcal{O}\left(P \Delta t^3 \right)$$

Since $P = t/\Delta t$, then the error at time t goes as Δt^2.

While, *per time step*:

$$e^{iL \Delta t} \approx e^{iL_2 \Delta t/2} e^{iL_1 \Delta t} e^{iL_2 \Delta t/2} + \mathcal{O}\left(\Delta t^3 \right)$$

Let's start from a classical Hamiltonian

$$\mathcal{H} = p^2/2m + U(x)$$

$$e^{iL\Delta t} \approx e^{iL_2\Delta t/2}e^{iL_1\Delta t}e^{iL_2\Delta t/2} + \mathcal{O}\left(\Delta t^3\right) \qquad iL_1 = \frac{p}{m}\frac{\partial}{\partial x} \qquad iL_2 = F(x)\frac{\partial}{\partial p}$$

$$\exp(iL\Delta t) \approx \exp\left(\frac{\Delta t}{2}F(x)\frac{\partial}{\partial p}\right)\exp\left(\Delta t\frac{p}{m}\frac{\partial}{\partial x}\right)\exp\left(\frac{\Delta t}{2}F(x)\frac{\partial}{\partial p}\right)$$

$$\begin{pmatrix} x(\Delta t) \\ p(\Delta t) \end{pmatrix} \approx \exp\left(\frac{\Delta t}{2}F(x(0))\frac{\partial}{\partial p(0)}\right) \times \exp\left(\Delta t\frac{p(0)}{m}\frac{\partial}{\partial x(0)}\right) \times \exp\left(\frac{\Delta t}{2}F(x(0))\frac{\partial}{\partial p(0)}\right)\begin{pmatrix} x(0) \\ p(0) \end{pmatrix}$$

Evaluation of the exponential operator:

$$\exp\left(c\frac{\partial}{\partial x}\right)g(x) = \sum_{k=0}^{\infty}\frac{1}{k!}\left(c\frac{\partial}{\partial x}\right)^k g(x) = \sum_{k=0}^{\infty}\frac{1}{k!}c^k g^{(k)}(x)$$

$$\Rightarrow \quad \exp\left(c\frac{\partial}{\partial x}\right)g(x) = g(x + c)$$

Liouville formulation: integrator for classical Hamiltonian

$$\begin{pmatrix} x(\Delta t) \\ p(\Delta t) \end{pmatrix} \approx \exp\left(\frac{\Delta t}{2}F(x(0))\frac{\partial}{\partial p(0)}\right) \times \exp\left(\Delta t\frac{p(0)}{m}\frac{\partial}{\partial x(0)}\right) \times \exp\left(\frac{\Delta t}{2}F(x(0))\frac{\partial}{\partial p(0)}\right)\begin{pmatrix} x(0) \\ p(0) \end{pmatrix}$$

$$\exp\left(c\frac{\partial}{\partial x}\right)g(x) = g(x+c)$$

Stepwise application of the Liouville operator for a classical Hamiltonian

$$\exp\left(\frac{\Delta t}{2}F(x)\frac{\partial}{\partial p}\right)\begin{pmatrix} x \\ p \end{pmatrix} = \begin{pmatrix} x \\ p + \frac{\Delta t}{2}F(x) \end{pmatrix}$$

$$\exp\left(\Delta t\frac{p}{m}\frac{\partial}{\partial x}\right)\begin{pmatrix} x \\ p + \frac{\Delta t}{2}F(x) \end{pmatrix} = \begin{pmatrix} x + \Delta t\frac{p}{m} \\ p + \frac{\Delta t}{2}F\left(x + \Delta t\frac{p}{m}\right) \end{pmatrix}$$

$$\exp\left(\Delta t F(x)\frac{\partial}{\partial p}\right)\begin{pmatrix} x + \Delta t\frac{p}{m} \\ p + \frac{\Delta t}{2}F\left(x + \Delta t\frac{p}{m}\right) \end{pmatrix} = \begin{pmatrix} x + \frac{\Delta t}{m}\left(p + \frac{\Delta t}{2}F(x)\right) \\ p + \frac{\Delta t}{2}F(x) + \frac{\Delta t}{2}F\left[x + \frac{\Delta t}{m}\left(p + \frac{\Delta t}{2}F(x)\right)\right] \end{pmatrix}$$

Liouville formulation: integrator for classical Hamiltonian

$$\exp\left(\frac{\Delta t}{2}F(x)\frac{\partial}{\partial p}\right)\begin{pmatrix} x \\ p \end{pmatrix} = \begin{pmatrix} x \\ p + \frac{\Delta t}{2}F(x) \end{pmatrix}$$

$$\exp\left(\Delta t\frac{p}{m}\frac{\partial}{\partial x}\right)\begin{pmatrix} x \\ p + \frac{\Delta t}{2}F(x) \end{pmatrix} = \begin{pmatrix} x + \Delta t\frac{p}{m} \\ p + \frac{\Delta t}{2}F\left(x + \Delta t\frac{p}{m}\right) \end{pmatrix}$$

$$\exp\left(\Delta t F(x)\frac{\partial}{\partial p}\right)\begin{pmatrix} x + \Delta t\frac{p}{m} \\ p + \frac{\Delta t}{2}F\left(x + \Delta t\frac{p}{m}\right) \end{pmatrix} = \begin{pmatrix} x + \frac{\Delta t}{m}\left(p + \frac{\Delta t}{2}F(x)\right) \\ p + \frac{\Delta t}{2}F(x) + \frac{\Delta t}{2}F\left[x + \frac{\Delta t}{m}\left(p + \frac{\Delta t}{2}F(x)\right)\right] \end{pmatrix}$$

$$x(\Delta t) = x(0) + \Delta t v(0) + \frac{\Delta t^2}{2m}F(x(0))$$

Velocity Verlet!

$$v(\Delta t) = v(0) + \frac{\Delta t}{2m}\left[F(x(0)) + F(x(\Delta t))\right]$$

Gives directly the implementation:

$$p(\Delta t/2) = p(0) + \frac{\Delta t}{2}F(x(0))$$

$$x(\Delta t) = x(0) + \frac{\Delta t}{m}p(\Delta t/2)$$
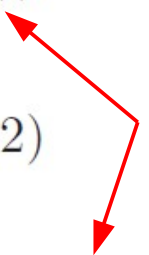
$$p(\Delta t) = p(\Delta t/2) + \frac{\Delta t}{2}F(x(\Delta t))$$

$$p = p + 0.5 * \Delta t * F$$

$$x = x + \Delta t * p/m$$

Recalculate the force

$$p = p + 0.5 * \Delta t * F.$$

Liouville formulation: multiple time-scale integrator

Hamiltonian with "fast" and "slow" degrees of freedom

$$\dot{x} = \frac{p}{m}$$

$$\dot{p} = F_{\text{fast}}(x) + F_{\text{slow}}(x)$$

$$iL = \frac{p}{m}\frac{\partial}{\partial x} + [F_{\text{fast}}(x) + F_{\text{slow}}(x)]\frac{\partial}{\partial p}$$

$$iL = iL_1 + iL_2$$

$$iL_1 = \frac{p}{m}\frac{\partial}{\partial x}$$

$$iL_2 = [F_{\text{fast}}(x) + F_{\text{slow}}(x)]\frac{\partial}{\partial p}$$

$$iL = iL_{\text{fast}} + iL_{\text{slow}}$$

$$iL_{\text{fast}} = \frac{p}{m}\frac{\partial}{\partial x} + F_{\text{fast}}(x)\frac{\partial}{\partial p}$$

$$iL_{\text{slow}} = F_{\text{slow}}(x)\frac{\partial}{\partial p}.$$

$$\exp(iL\Delta t) = \exp\left(iL_{\text{slow}}\frac{\Delta t}{2}\right)\exp(iL_{\text{fast}}\Delta t)\exp\left(iL_{\text{slow}}\frac{\Delta t}{2}\right)$$

Introduction of a sub-timestep $\delta t = \Delta t/n$

$$\exp(iL_{\text{fast}}\Delta t) = \left[\exp\left(\frac{\delta t}{2}F_{\text{fast}}\frac{\partial}{\partial p}\right)\exp\left(\delta t\frac{p}{m}\frac{\partial}{\partial x}\right)\exp\left(\frac{\delta t}{2}F_{\text{fast}}\frac{\partial}{\partial p}\right)\right]^n$$

$$\exp(iL\Delta t) = \exp\left(\frac{\Delta t}{2}F_{\text{slow}}\frac{\partial}{\partial p}\right)\left[\exp\left(\frac{\delta t}{2}F_{\text{fast}}\frac{\partial}{\partial p}\right)\exp\left(\delta t\frac{p}{m}\frac{\partial}{\partial x}\right)\exp\left(\frac{\delta t}{2}F_{\text{fast}}\frac{\partial}{\partial p}\right)\right]^n$$

$$\times \exp\left(\frac{\Delta t}{2}F_{\text{slow}}\frac{\partial}{\partial p}\right)$$

$p = p + 0.5 * \Delta t * F_{\text{slow}}$
for i $= 1$ to n
$\quad p = p + 0.5 * \delta t * F_{\text{fast}}$
$\quad x = x + \delta t * p/m$
$\quad$ Recalculate fast force
$\quad p = p + 0.5 * \delta t * F_{\text{fast}}$
endfor
Recalculate slow force
$p = p + 0.5 * \Delta t * F_{\text{slow}}.$

Outline

- Basic MD
- Chaos
- Shadow trajectories
- Ergodicity

- Practical MD

- Ensembles
- MD generates the NVE ensemble
- The canonical NVT ensemble: thermostats

- Integrating the equations of motion
- Verlet or velocity Verlet?
- Liouville formulation
- Multiple time steps

- Applications:
- Vibrations
- Computing transport properties

Calculating vibrations via MD

Time autocorrelation functions can give information about vibrations
– From Fermi's golden rule, the dipole time auto correlation
function gives the intensities of IR active frequencies

$$I(\omega) = \int_{-\infty}^{\infty} dt \, e^{i\omega t} \langle \vec{M}(t) \cdot \vec{M}(0) \rangle_t$$

Electric dipole moment

– Velocity time autocorrelation gives all frequencies of vibration.

$$\text{VDOS}(\omega) = \sum_{i=1}^{N} \int_{-\infty}^{\infty} dt \, e^{i\omega t} \langle \vec{v}_i(t) \cdot \vec{v}_i(0) \rangle_t$$

– Possible to assign to individual atoms displacements and project on eigenmodes.

LMG *et al.* NJP (2013)

LMG *et al.* NJP (2013)
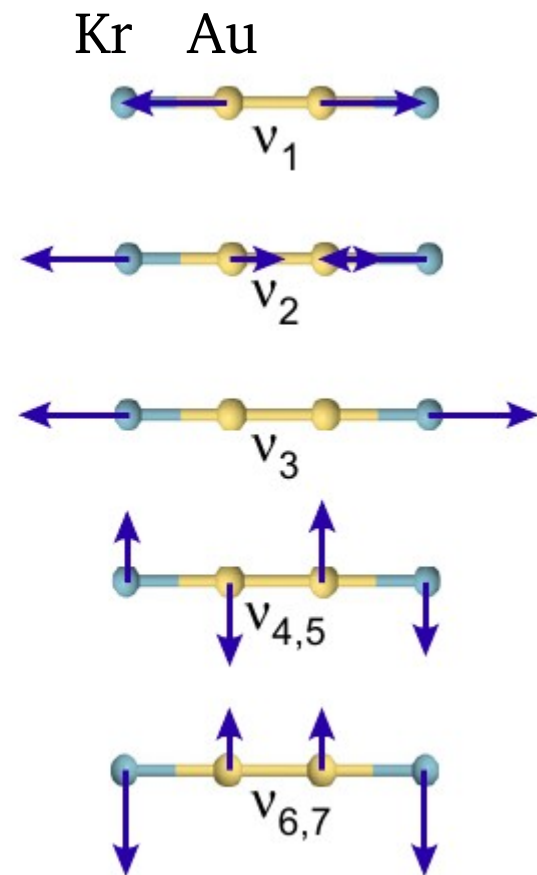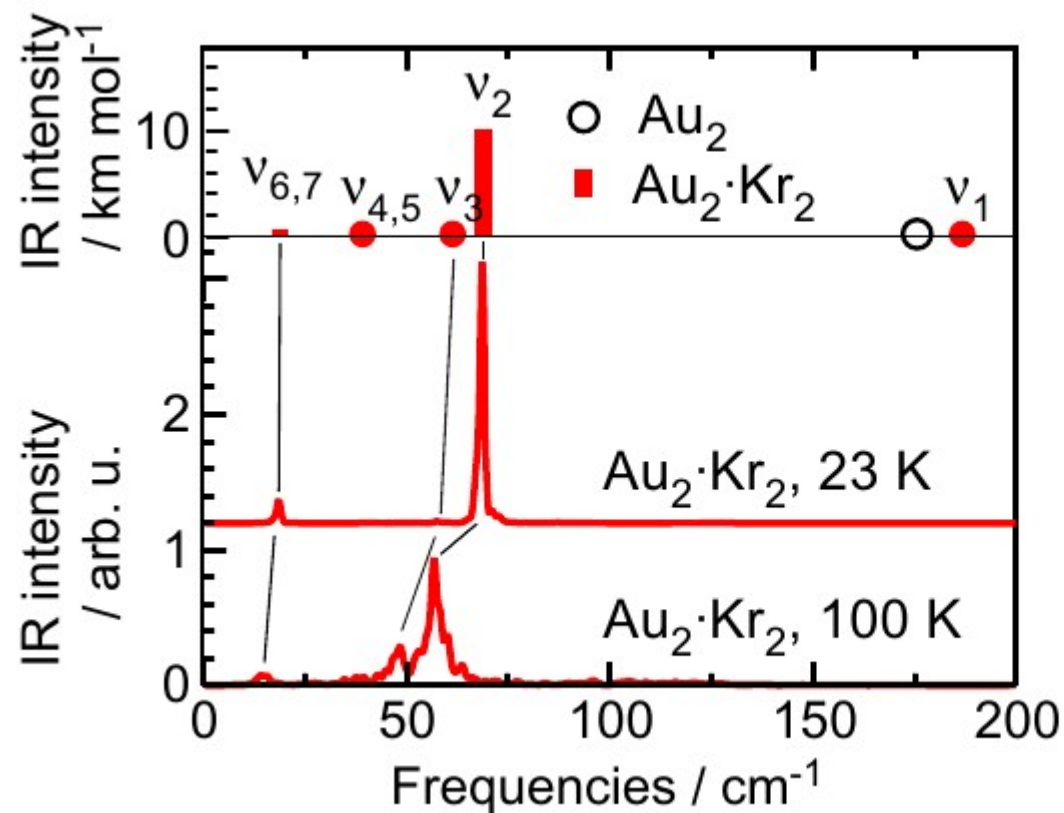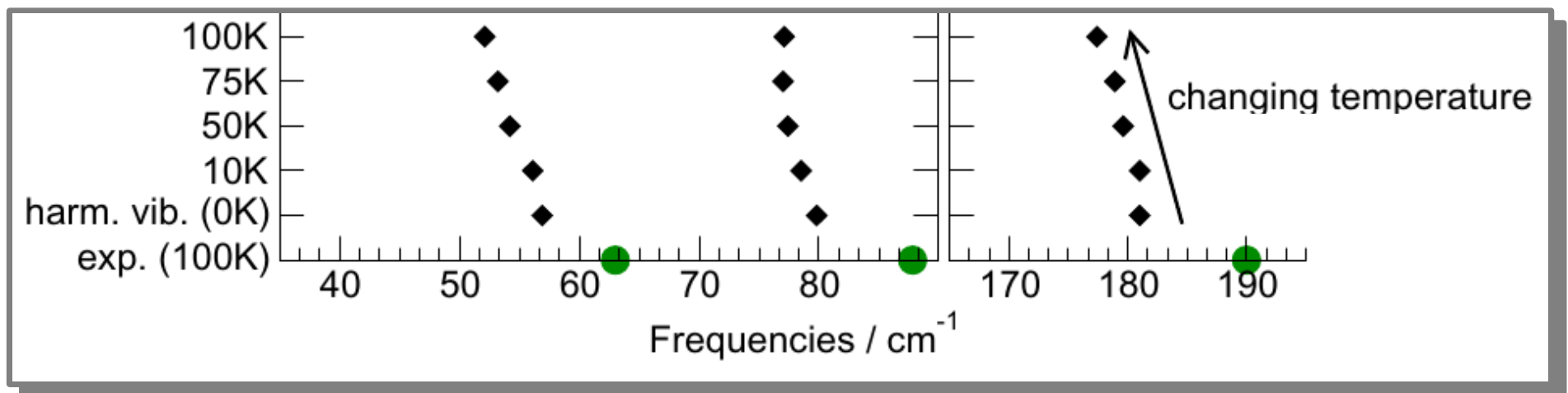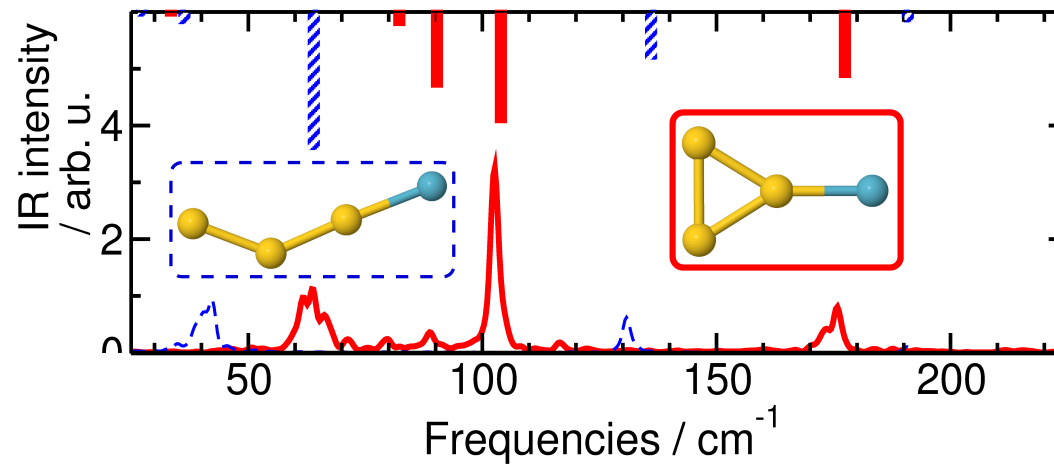
Vibrational spectroscopy: Ac-Ala$_{15}$-LysH$^+$

Rossi et al., JCP Lett. (2010)

α-helical Ac-Ala$_{15}$-LysH$^+$
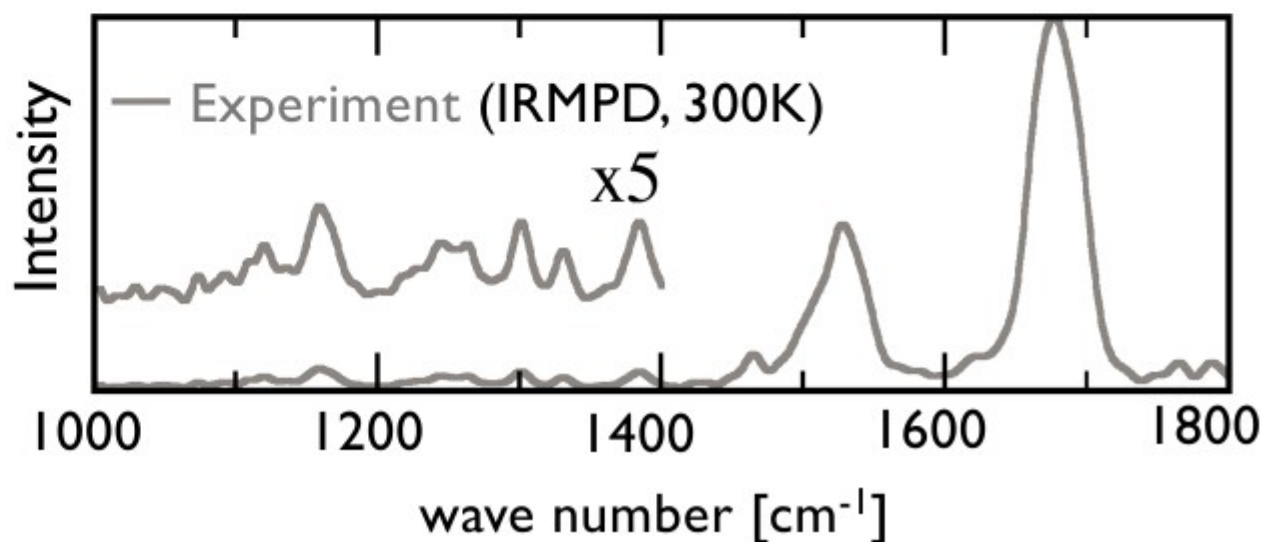
Experiment:
von Helden, Kupser, Bierau, Meijer,
Molecular Physics, FHI Berlin

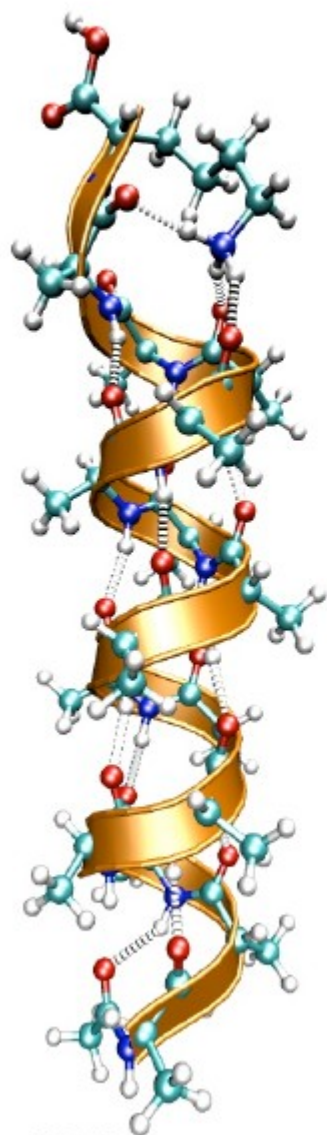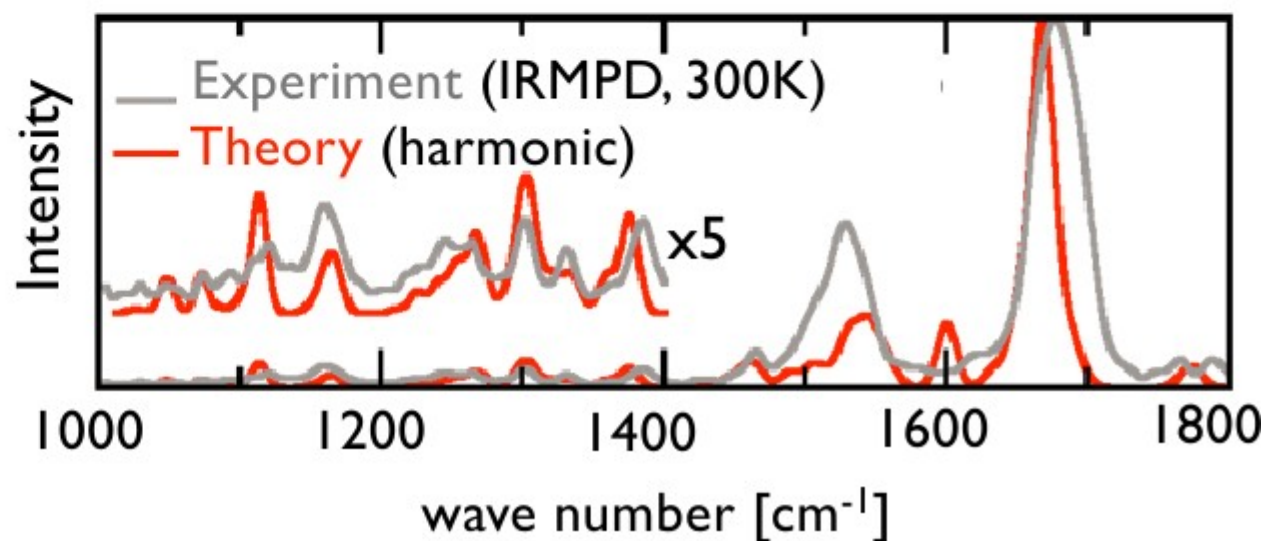Infrared multiphoton dissociation
spectroscopy, FELIX free electron laser

Room temperature

180 atoms

Rossi et al., JCP Lett. (2010)

α-helical Ac-Ala$_{15}$-LysH$^+$
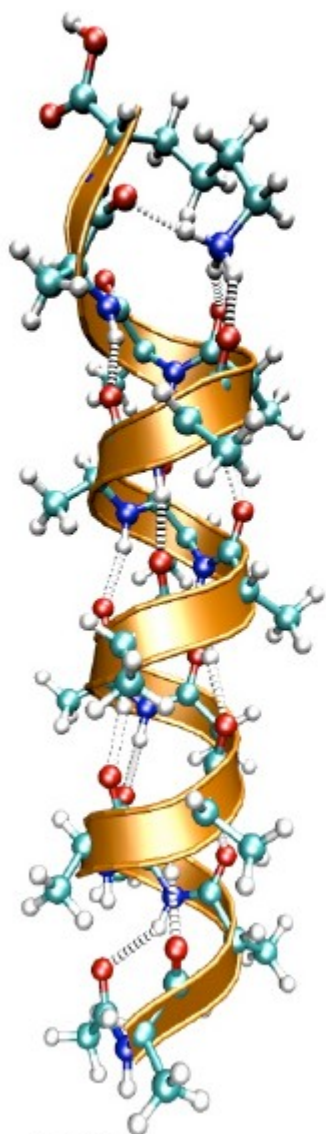
180 atoms

Experiment:
von Helden, Kupser, Bierau, Meijer,
Molecular Physics, FHI Berlin

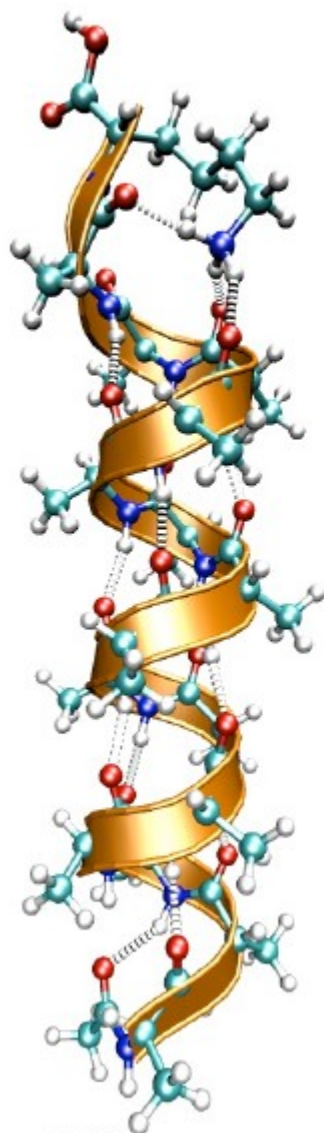Infrared multiphoton dissociation
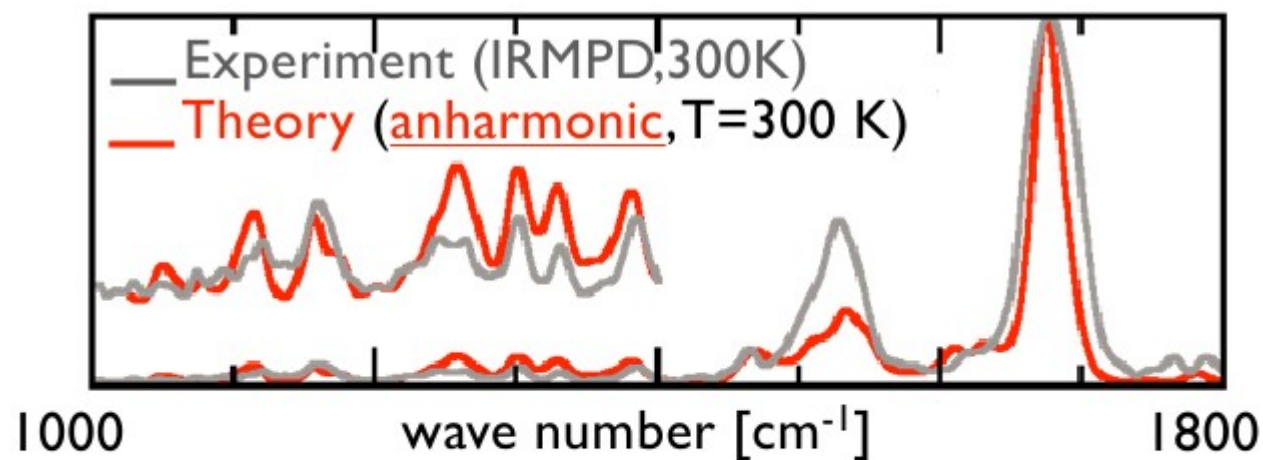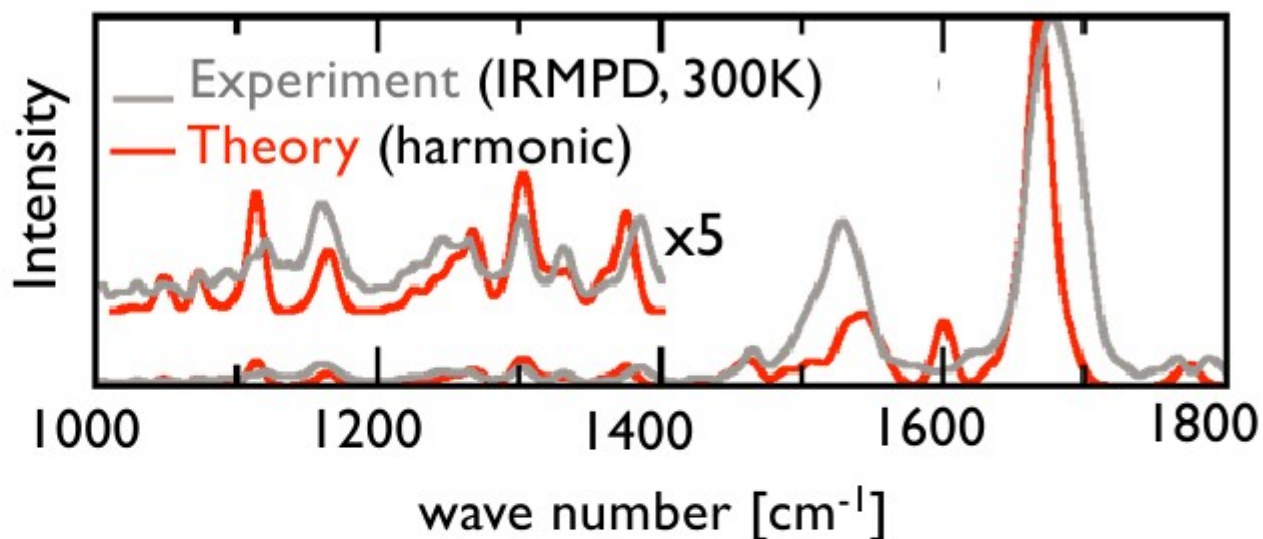spectroscopy, FELIX free electron laser

Room temperature

Experiment (IRMPD, 300K)
Theory (harmonic)
x5

wave number [cm^{-1}]

α-helical Ac-Ala₁₅-LysH⁺
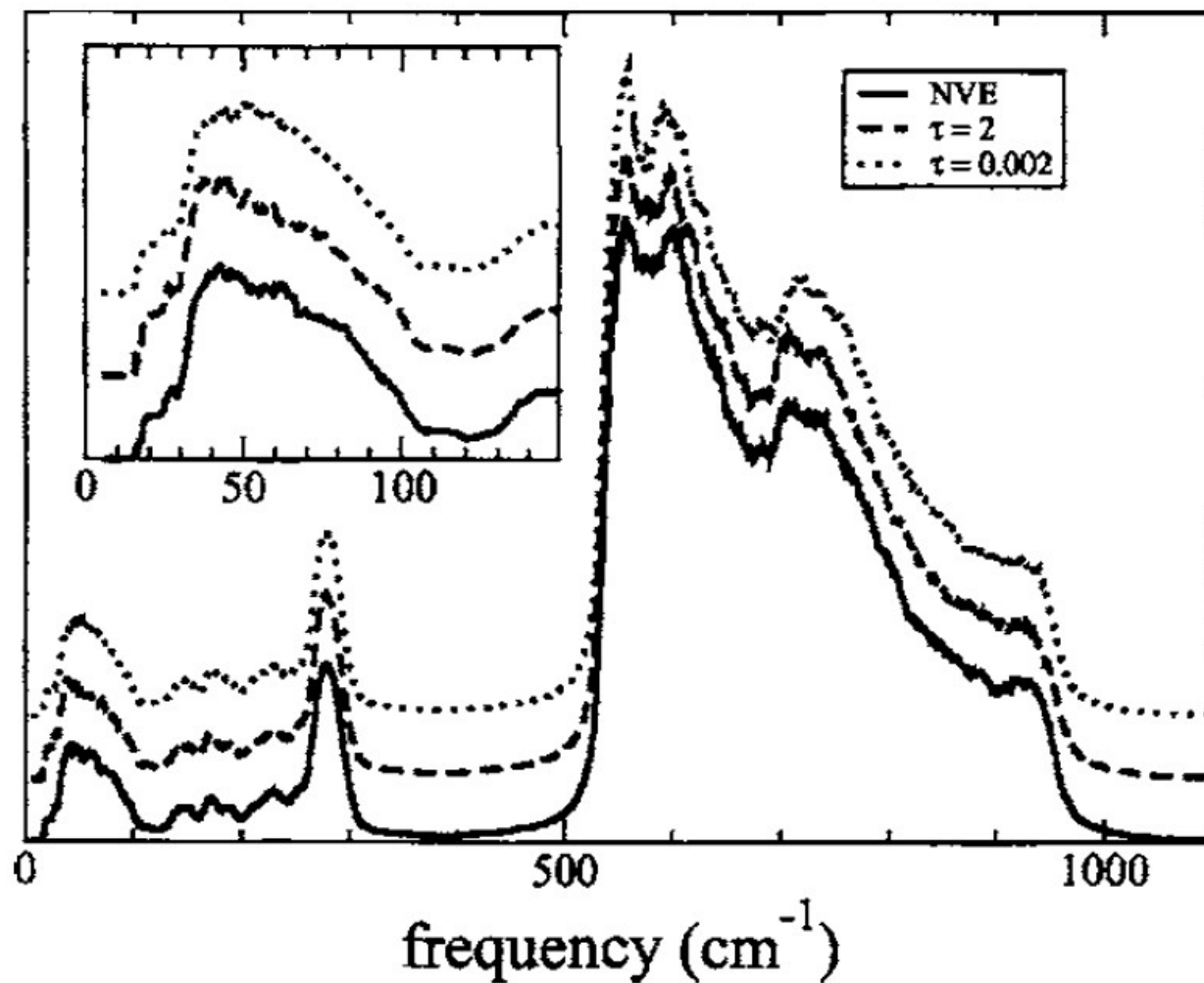
Rossi et al., JCP Lett. (2010)

180 atoms

$$I(\omega) \propto \omega^2 \int_{-\infty}^{\infty} dt \underbrace{\langle \vec{M}(t) \cdot \vec{M}(0) \rangle}_{} e^{iwt}$$

dipole-dipole time correlation function

Vibrational density of states of proton (H) in ice

Bussi, Donadio, Parrinello JCP (2007)

Diffusion equation (Fick's second law)

$$\frac{\partial c(x,t)}{\partial t} = D \frac{\partial^2 c(x,t)}{\partial x^2}$$

Solution for an initial $c(x,0) = \delta(0)$: all molecules at origin

$$c(x,t) = \frac{1}{\sqrt{4\pi D t}} \exp\left(-\frac{x^2}{4Dt}\right)$$

Mean square displacement of the molecules

$$\langle x^2(t) \rangle = \frac{\int dx\, x^2 c(x,t)}{\int dx\, c(x,t)} = \int dx \frac{x^2 e^{-\frac{x^2}{4Dt}}}{\sqrt{4\pi D t}} = 2Dt$$

Time derivative gives

$$2D = \lim_{t\to\infty} \frac{d\langle x^2(t) \rangle}{dt}$$

Transport coefficients: Diffusion

General $c(x,t)$

$$\frac{\partial}{\partial t} \int dx \; x^2 c(x,t) = D \int dx \; x^2 \frac{\partial^2 c(x,t)}{\partial x^2}$$

$$2D = \lim_{t \to \infty} \frac{d\langle x^2(t) \rangle}{dt}$$

Diffusion in 3 dimensions

$$\boxed{D = \frac{1}{6} \lim_{t \to \infty} \frac{d\langle \mathbf{r}^2(t) \rangle}{dt}}$$

Relation to velocity:

$$\Delta x(t) = \int_0^t dt' \; v_x(t')$$

$$\langle x^2(t) \rangle = \left\langle \left(\int_0^t dt' \; v_x(t') \right)^2 \right\rangle$$

$$= \int_0^t \int_0^t dt' dt'' \; \langle v_x(t') v_x(t'') \rangle$$

$$= 2 \int_0^t \int_0^{t'} dt' dt'' \; \langle v_x(t') v_x(t'') \rangle$$

Transport coefficients: Diffusion

$$\frac{\partial \langle x^2(t) \rangle}{\partial t} = 2\frac{\partial}{\partial t} \int_0^t dt' \int_0^{t'} dt'' \langle v_x(t') v_x(t'') \rangle$$

$$\langle v_x(t') v_x(t'') \rangle = \langle v_x(t' - t'') v_x(0) \rangle$$

$$2D = \lim_{t \to \infty} 2 \int_0^t dt'' \langle v_x(t - t'') v_x(0) \rangle$$

Define: $\tau = t - t''$

$$D = \int_0^\infty d\tau \; \langle v_x(\tau) v_x(0) \rangle$$

Green –Kubo relation
Also exists for other transport coefficients, such as viscosity and conductivity

MD generates the microcanonical (*NVE*) ensemble

In general the microcanonical phase space density is

$$\rho(x) = e^{-\beta \mathcal{H}(x)}/Z \qquad Z = \int e^{-\beta \mathcal{H}(x)} dx$$

with $x = \{p^N, r^N\}$

Integration over momenta gives

$$Z = \frac{1}{N! \Lambda^{3N}} \int e^{-\beta \mathcal{U}(r)} dr$$

N! comes from indistinguishability of particles.
But MD conserves Hamiltonian H= E = constant (and constant total P).

$$\rho(x) = \delta[E - \mathcal{H}(x)]/g(E) \qquad g(E) = \int dx \delta[E - \mathcal{H}(x)]$$

with instantaneous temperature $k_B T = \sum_{i=1}^{N} \frac{m v_i^2}{N_f}$